HDS ACTIVITY AND SURFACE PROPERTY
OF ALUMINA-SUPPORTED RUTHENIUM CATALYST

Masatoshi Nagai and Kenji Koizumi
Department of Chemical Engineering,
Tokyo University of Agriculture and Technology,
Koganei, Tokyo 184, Japan

INTRODUCTION

Ruthenium and its compounds have wide ranging application in both heterogeneous and homogeneous catalysis. Recent environmental and economic problems offer a challenge for developing new catalysts capable of deep hydrodesulfurization (HDS) and hydrogenation of aromatics in the presence of sulfur and nitrogen compounds. Unsupported ruthenium sulfides were reported to show a high activity for HDS and hydrogenation (1,2). The catalytic activity for HDS reaction is likely to depend upon greatly the preparation and pretreatment of the ruthenium catalysts, such as surface composition, surface acidity, and electronic property of ruthenium (3,4). The objective of this study was to report the effects of catalyst pretreatment on the catalytic activity of an alumina-supported ruthenium catalyst for thiophene HDS.

EXPERIMENTAL

0.49% Ru/Al_2O_3 (JRC-A4-0.5Ru2) was prepared by impregnation of alumina powder with aqueous solution of ruthenium trichloride. 0.2 g of catalyst was charged to the reactor for a typical series of experiments. The Ru/Al_2O_3 catalyst was pretreated with three ways prior to catalyst characterization and activity measurement; reduced in H_2 for 4 h (Ru-R catalyst), oxidized in air at 400 $^{\circ}$C for 3 h, following reduction in H_2 for 4 h (Ru-OR catalyst), or sulfided in a 10 % H_2S/H_2 stream (Ru-S catalyst). The HDS activity measurement for thiophene HDS was carried out in a continuous-flow microreactor.

The surface property of the catalyst was measured by NH_3-TPD, H_2 adsorption, XPS, and in-situ DRIFT FT-IR spectroscopy. For the NH_3-TPD experiment, the catalyst was heated to 500 $^{\circ}$C at a rate of 10 $^{\circ}$C/min under He flow. It was maintained under these conditions for 1 h and then slowly cooled to room temperature. The He flow was switched to a 5.1% NH_3/He flow to adsorb NH_3 to the catalyst. The catalyst was heated at a rate of 10 $^{\circ}$C/min to 500 $^{\circ}$C (or 600 $^{\circ}$C) under He flow. The outlet gas was analyzed by either a gas chromatograph or a quadrupole mass spectrometer with a valunarable-leak valve. Hydrogen adsorption was analyzed by a thermal conductive detector of a gas chromatograph after the pretreatment. The H_2 uptake was measured using pulses of 10 % H_2/He to the reactor at room temperature. The surface composition of the catalyst was measured by X-ray photoelectron spectroscopy.

RESULTS AND DISCUSSION

The physical properties and HDS activity of the catalyst are shown in Table 1. The Ru-S300 catalyst was the most active of the all catalysts for thiophene HDS, but the Ru-S400 catalyst had lowest activity. The Ru-OR300 catalyst was more active than the Ru-R200 and Ru-R400 catalysts.

Three kinds of peaks (low-, middle-, and high-temperature) were observed in NH_3-TPD profile. The Ru-S300 and Ru-OR300 catalysts have a predominant high-temperature peak with a small low-temperature peak. However, the Ru-S400, Ru-R200 and Ru-R400 catalysts have no high-temperature peaks, but middle-temperature peaks together with a small low-temperature peak. Alumina support has only middle-temperature peaks in the NH_3-TPD profile. Mass spectroscopy and XPS analyses showed that the low-, middle- and high-temperature peaks were assigned to RuO_2 (280.7-281.1 eV), acid sites on alumina, and Ru metal (280.2 eV),

respectively (5,6). The spectra at 280.2 eV was not observed for the fresh catalyst but for the reduced and sulfided catalysts.

The HDS activity was not concerned with low-temperature peak of NH_3-TPD, but high-temperature peak. The high-temperature peak of NH_3-TPD was related to H_2 adsorption and the intensity of XPS Ru3d spectra at 280.3 eV (Ru metal).

The particle size was determined by H_2 chemisorption at room temperature. The Ru-R300 catalyst had smaller particles than the Ru-R400 catalyst. The selectivity of the Ru/Al_2O_3 catalyst for hydrogenation of butenes to butane in thiophene HDS was calculated. The ratio of butane/butenes indicated the hydrogenation activity. The ratio for the Ru-R400 catalyst was higher than that for the Ru-R300 catalyst. The ratio of butane/butenes in the products was increased with increasing particle size for the catalyst. The selectivity of the Ru-R400 catalyst was more than the Ru-R300 catalyst for the hydrogenation of butenes to butane. Since the particle size of the Ru-R400 catalyst was larger than that of the Ru-R300, the large Ru particle of the catalyst appeared to facilitate the hydrogenation of butenes to butane. The particle size was concerned with the selectivity of butane/butanes (hydrogenation) in the reaction.

LITERATURE CITED

(1) Pecoraro, T. A., and Chianelli, R. R., J. Catal. **67** 430 (1981).
(2) Lacroix, M., Boutarfa, N., Guillard, C., Vrinat, M., and Breysse, M., J. Catal. **120**, 473 (1989).
(3) Cocco, A., and Tatarchuk, B. J., Langmuir **2**, 1309 (1989).
(4) Lu, K., and Tatarchuk, B. J., J. Catal. **106**, 166 (1987).
(5) De los Reyes, J. A., Gobilos, S., Vrinat, M., and Breysse, M., Grimblot, J., J. Catal. **142**, 455 (1993).
(6) Mitchell, P. C. H., Scott, C. E., Bonnelle, J.-P., Grimblot, J. G., J. Catal. 107, **482** (1987).

Table 1. Surface property and HDS activity of Ru/Al_2O_3 Catalyst

Catalyst	Pretreatment Temp.			Conversion	Amount of adsorbed H_2 [10^{-2}ml/g]	Ru particle size [nm]	NH_3-TPD[4]		
	Oxi[1]	Red[2]	Sul[3]	[%]			LTP	MTP	HTP
							[°C]		
Ru-OR300	400	300	–	37.5	6.8	2.6	167s	327m	427s
Ru-OR400	400	400	–	14.6	2.2	7.6	192s	321m	
Ru-R300	–	300	–	51.5	1.2	4.5	200w	300m	
Ru-R400	–	400	–	8.8	1.0	22.9	200w	300m	
Ru-S300	–	–	300	13.9	8.9	2.0	178s	364m	418s
Ru-S400	–	–	400	4.9	0.8	26.6	186w	330w	

1)Oxidation, 2)Reduction, 3)Sulfidation, 4)LTP, MTP, HTP, and w, m and s represent low-, middle-, and high-temperature peak, and weak, middle and strong intensity, respectively.